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(57) Abstract

This invention relates to a composition, comprising: (A) at least one basic alkali or alkaline earth metal salt of an acidic organic compound; (B) at least one metal deactivator other than dimercaptothiadiazole or derivatives thereof; and (C) at least one hydrocarbyl phosphite, wherein the ratio of the equivalents of (A) based on the total base number to the equivalents of (C) based on phosphorus atoms is at least one, provided that the composition is free of zinc dithiophosphate and provided that when (A) is an overbased magnesium salicylate then the composition contains (D) up to about 0.40 % by weight of a sulfur-, phosphorus-, or sulfur- and phosphorus-containing antiwear agent. These compositions are useful as additives for lubricants and functional fluids, particularly hydraulic fluids, gear oils, greases and the like. The lubricants and fluids having this particular combination of components have improved thermal stability and do not contain zinc dithiophosphate. These lubricants and fluids are also not corrosive to the hydraulic system components.

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THERMALLY STABLE COMPOSITIONS AND LUBRICANTS AND FUNCTIONAL FLUIDS CONTAINING THE SAME

Technical Field of the Invention

This invention relates to compositions which are useful as additives for lubricants and functional fluids. These additives provide lubricants and functional fluids with thermal stability and improved antiwear, extreme pressure, load-carrying and/or corrosion-inhibiting properties.

Introduction to the Invention

Historically antiwear hydraulic fluids have contained zinc in the form of zinc dithiophosphates. These hydraulic fluids typically have excellent thermal stability and antiwear properties. However, in recent years there has been growing concern about the accumulation in the work place and environment of heavy metals such as zinc. This concern has lead to the demand for hydraulic fluids which contain only ashless antiwear agents. Ashless antiwear agents are available but often fluids containing these agents lack thermal stability. One test which measures a lubricant's thermal stability is the Cincinnati Milicron test.

Hydrocarbyl phosphites are antiwear agents which are useful in replacing zinc dithiophosphates in hydraulic fluids. However, under high temperature operating conditions, phosphites form products which are corrosive to the yellow metal components in the hydraulic systems. Without a means to stabilize phosphites, they are ineffective in replacing zinc dithiophosphates in hydraulic fluids.

PCT publication WO 89/04358 relates to a composition comprising (A) a neutral or basic metal salt or boron-containing neutral or basic metal salt of at least one acidic organic compound, (B) a metal deactivator and (C) a sulfur- and/or phosphorus-containing compound. These compositions are used in lubricants and functional fluids.

Summary of the Invention

This invention relates to a composition, comprising:

(A) at least one basic alkali or alkaline earth metal salt of an acidic organic compound;

(B) at least one metal deactivator other than dimercaptothiadiazole or derivatives thereof; and

(C) at least one hydrocarbyl phosphite, wherein the equivalents of (A) based on total base number to the equivalents of (C) based on phosphorus atoms is at least one,

provided that the composition is free of zinc dithiophosphate and

provided that when (A) is an overbased magnesium salicylate then the composition contains (D) up to about 0.40% by weight of a sulfur-, phosphorus-, or sulfur- and phosphorus-containing antiwear agent. These compositions are useful as additives for lubricants and functional fluids, particularly hydraulic fluids, gear oils, greases and the like. The lubricants and fluids having this particular combination of components have improved thermal stability and do not contain zinc dithiophosphate. These lubricants and fluids are also not corrosive to the hydraulic system components.

Description of the Invention

The term "hydrocarbyl" includes hydrocarbon, as well as substantially hydrocarbon, groups. Substantially hydrocarbon describes groups which contain non-hydrocarbon substituents which do not alter the predominately hydrocarbon nature of the group.

Examples of hydrocarbyl groups include the following:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and

alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.);

(3) hetero substituents, that is, substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain other than carbon present in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc. In general, no more than about 2, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such non-hydrocarbon substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

(A) Basic Metal Salts

The lubricating compositions of the present invention contain (A) at least one basic alkali or alkaline earth metal salt of an acidic organic compound. These salts are generally referred to as overbased materials. Overbased materials are single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present according to the stoichiometry of

the metal and the particular acidic organic compound reacted with the metal.

The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The basic salts of the present invention have a metal ratio of about 1.5, more preferably about 3, more preferably about 7, up to about 40, preferably about 25, more preferably about 20.

The basicity of the overbased materials of the present invention generally is expressed in terms of a total base number. A total base number is the amount of acid (perchloric or hydrochloric) needed to neutralize all of the overbased material's basicity. The amount of acid is expressed as potassium hydroxide equivalents. Total base number is determined by titration of one gram of overbased material with 0.1 Normal hydrochloric acid solution using bromophenolblue as an indicator. The overbased materials of the present invention generally have a total base number of at least about 20, preferably about 100, more preferably about 200. The overbased material generally have a total base number up to about 600, preferably about 500, more preferably about 400. The total base number is essential to the invention because the inventors have discovered that the ratio of the equivalents of overbased material based on total base number to the equivalents of hydrocarbyl phosphite based on phosphorus atoms must be at least one to make the thermally stable lubricating compositions of the present invention. The equivalents of overbased material is determined by the following equation: equivalent weight = (56,100/total base number). For instance, an overbased material with a total

base number of 200 has an equivalent weight of 280.5 (eqwt = 56100/200). The equivalents of phosphite are determined by dividing the molecular weight of the phosphite by the number of phosphorus atoms in the phosphite.

The overbased materials (A) are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter.

The acidic organic compounds useful in making the overbased compositions of the present invention include carboxylic acids, sulfonic acids, phosphorus-containing acids, phenols or mixtures of two or more thereof. Preferably, the acidic organic compounds are carboxylic acids or sulfonic acids with sulfonic and salicylic acids more preferred. Throughout this specification and in the appended claims, any reference to acids, such as carboxylic, or sulfonic acids, is intended to include the acid-producing derivatives thereof such as anhydrides, lower alkyl esters, acyl halides, lactones and mixtures thereof unless otherwise specifically stated.

The carboxylic acids useful in making the overbased salts (A) of the invention may be aliphatic or aromatic, mono- or polycarboxylic acid or acid-producing compounds. These carboxylic acids include lower molecular weight carboxylic acids (e.g., carboxylic acids having up to about 22 carbon atoms such as acids having about 4 to about 22 carbon atoms or tetrapropenyl-substituted succinic anhydride) as well as higher molecular weight carboxylic acids.

The carboxylic acids of this invention are preferably oil-soluble. Usually, in order to provide the

desired oil-solubility, the number of carbon atoms in the carboxylic acid should be at least about 8, more preferably at least about 18, more preferably at least about 30, more preferably at least about 50. Generally, these carboxylic acids do not contain more than about 400 carbon atoms per molecule.

The lower molecular weight monocarboxylic acids contemplated for use in this invention include saturated and unsaturated acids. Examples of such useful acids include dodecanoic acid, decanoic acid, oleic acid, stearic acid, linoleic acid, tall oil acid, etc. Mixtures of two or more such agents can also be used. An extensive discussion of these acids is found in Kirk- Othmer "Encyclopedia of Chemical Technology" Third Edition, 1978, John Wiley & Sons New York, pp. 814-871; these pages being incorporated herein by reference.

The monocarboxylic acids include isoaliphatic acids. Such acids often contain a principal chain having from about 14 to about 20 saturated, aliphatic carbon atoms and at least one but usually no more than about four pendant acyclic lower alkyl groups. Specific examples of such isoaliphatic acids include 10-methyl-tetradecanoic acid, 3-ethyl-hexadecanoic acid, and 8-methyl-octadecanoic acid. The isoaliphatic acids include mixtures of branch-chain acids prepared by the isomerization of commercial fatty acids (oleic, linoleic or tall oil acids) of, for example, about 16 to about 20 carbon atoms.

High molecular weight carboxylic acids may also be used in the present invention. These acids have a substituent group derived from a polyalkene. The polyalkene is characterized as containing at least about 30 carbon atoms, preferably at least about 35, more preferably at least about 50, and up to about 300 carbon atoms, preferably about 200, more preferably about 150. In one embodiment, the polyalkene is characterized by an Mn (number

average molecular weight) value of at least about 500, generally about 500 to about 5000, preferably about 800 to about 2500. In another embodiment, Mn varies between about 500 to about 1200 or 1300.

The polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, preferably diolefinic, monomer such 1,3-butadiene and isoprene. Preferably the monomers contain from 2 to about 6 carbon atoms, more preferably 2 to about 4, more preferably 4. The interpolymers include copolymers, terpolymers, tetrapolymers and the like. Preferably, the interpolymer is a homopolymer. An example of a preferred homopolymer is a polybutene, preferably a polybutene in which about 50% of the polymer is derived from isobutylene. The polyalkenes are prepared by conventional procedures.

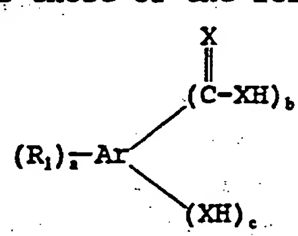
The higher molecular weight mono- and polycarboxylic acids suitable for use in making the overbased salts (A) are well known in the art and have been described in detail, for example, in the following U.S., British and Canadian patents: U.S. Patents 3,024,237; 3,172,892; 3,219,666; 3,245,910; 3,271,310; 3,272,746; 3,278,550; 3,306,907; 3,312,619; 3,341,542; 3,367,943; 3,374,174; 3,381,022; 3,454,607; 3,470,098; 3,630,902; 3,755,169; 3,912,764; and 4,368,133; British Patents 944,136; 1,085,903; 1,162,436; and 1,440,219; and Canadian Patent 956,397. These patents are incorporated herein by reference for their disclosure of higher molecular weight mono- and polycarboxylic acids and methods for making the same.

Illustrative carboxylic acids include palmitic acid, stearic acid, myristic acid, oleic acid, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropylenyl-substituted glutaric acid, polybutenyl-substituted

succinic acid derived from a polybutene (Mn = 200-1500, preferably 300-1000), polypropenyl-substituted succinic acid derived from a polypropene, (Mn = 200-1000, preferably 300-900), octadecyl-substituted adipic acid, chlorostearic acid, 9-methylstearic acid, dichlorostearic acid, stearylbenzoic acid, eicosanyl-substituted naphthoic acid, dilauryl-decahydronaphthalene carboxylic acid, mixtures of any of these acids, their alkali and alkaline earth metal salts, and/or their anhydrides. A preferred group of aliphatic carboxylic acids includes the saturated and unsaturated higher fatty acids containing from about 12 to about 30 carbon atoms. Illustrative of these acids are lauric acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, oleostearic acid, stearic acid, myristic acid, and undecalinic acid, alpha-chlorostearic acid, and alphanitrolauric acid.

In another embodiment, the carboxylic acid is an alkylalkyleneglycol-acetic acid, more preferably alkylpolyethyleneglycol-acetic acid. Some specific examples of these compounds include: iso-stearylpentaethyleneglycol-acetic acid; iso-stearyl-O-$(CH_2CH_2O)_5CH_2CO_2Na$; lauryl-O-$(CH_2CH_2O)_{2.5}$-CH_2CO_2H; lauryl-O-$(CH_2CH_2O)_{3.3}CH_2CO_2H$; oleyl-O-$(CH_2CH_2O)_4$-$CH_2CO_2H$; lauryl-O-$(CH_2CH_2O)_{4.5}CH_2CO_2H$; lauryl-O-$(CH_2CH_2O)_{10}$-$CH_2CO_2H$; lauryl-O-$(CH_2CH_2O)_{16}CH_2CO_2H$; octyl-phenyl-O-$(CH_2CH_2O)_8$-$CH_2CO_2H$; octyl-phenyl-O-$(CH_2CH_2O)_{19}CH_2CO_2H$; 2-octyl-decanyl-O-$(CH_2CH_2O)_6CH_2CO_2H$. These acids are available commercially from Sandoz Chemical under the tradename Sandopan acids.

In another embodiment, the carboxylic acids are aromatic carboxylic acids. A group of useful aromatic carboxylic acids are those of the formula



wherein R_1 is an aliphatic hydrocarbyl group of preferably about 4 to about 400 carbon atoms, a is a number in the range of zero to about 4, usually 1 or 2, Ar is an aromatic group, each X is independently sulfur or oxygen, preferably oxygen, b is a number in the range of from 1 to about 4, usually 1 or 2, c is a number in the range of zero to about 4, usually 1 to 2, with the proviso that the sum of a, b and c does not exceed the number of valences of Ar. Preferably, R_1 and a are such that there is an average of at least about 8 aliphatic carbon atoms provided by the R_1 groups. Examples of aromatic carboxylic acids include substituted and non-substituted benzoic, phthalic and salicylic acids or anhydrides.

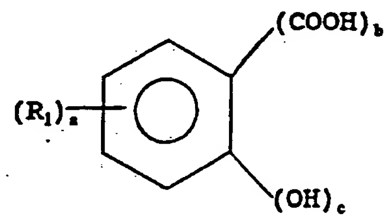
The R_1 group is a hydrocarbyl group that is directly bonded to the aromatic group Ar. R_1 preferably contains about 6 to about 80 carbon atoms, preferably about 6 to about 30 carbon atoms, more preferably about 8 to about 25 carbon atoms, and advantageously about 8 to about 15 carbon atoms. R_1 groups may be derived form one or more of the above-described polyalkenes. Examples of R_1 groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, 5-chlorohexyl, 4-ethoxypentyl, 3-cyclohexyloctyl, 2,3,5-trimethylheptyl, and substituents derived from polymerized olefins such as polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, chlorinated olefin polymers, oxidized ethylene-propylene copolymers, propylene tetramer and tri(isobutene).

Examples of the R_1 groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, and substituents derived from the above-described polyalkenes such as polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, oxidized ethylene-propylene copolymers, and the like.

The aromatic group Ar may have the same structure as any of the aromatic groups Ar discussed below. Examples

of the aromatic groups that are useful herein include the polyvalent aromatic groups derived from benzene, naphthalene, anthracene, etc., preferably benzene. Specific examples of Ar groups include phenylenes and naphthylene, e.g., methylphenylenes, ethoxyphenylenes, isopropylphenylenes, hydroxyphenylenes, dipropoxynaphthylenes, etc.

Within this group of aromatic acids, a useful class of carboxylic acids are those of the formula



wherein R_1 is defined above, a is a number in the range of from zero to about 4, preferably 1 to about 2; b is a number in the range of 1 to about 4, preferably 1 to about 2, c is a number in the range of zero to about 4, preferably 1 to about 2, and more preferably 1; with the proviso that the sum of a, b and c does not exceed 6. Preferably, R_1 and a are such that the acid molecules contain at least an average of about 12 aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule. Preferably, b and c are each one and the carboxylic acid is a salicylic acid.

The salicylic acids can be aliphatic hydrocarbon-substituted salicyclic acids wherein each aliphatic hydrocarbon substituent contains an average of at least about 8 carbon atoms per substituent and 1 to 3 substituents per molecule. Overbased salts prepared from such salicyclic acids wherein the aliphatic hydrocarbon substituents are derived from the above-described polyalkenes, particularly polymerized lower 1-mono-olefins such as polyethylene, polypropylene, polyisobutylene, ethylene/propylene copoly-

mers and the like and having average carbon contents of about 30 to about 400 carbon atoms are particularly useful.

The above aromatic carboxylic acids are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791.

The sulfonic acids useful in making the overbased salts (A) of the invention include the sulfonic and thiosulfonic acids. Generally they are salts of sulfonic acids. The sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonates can be represented for the most part by one of the following formulae: R_2-T-$(SO_3)_a$ and R_3-$(SO_3)_b$, wherein T is a cyclic nucleus such as, for example, benzene, naphthalene, anthracene, diphenylene oxide, diphenylene sulfide, petroleum naphthenes, etc.; R_2 is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, etc.; (R_2)+T contains a total of at least about 15 carbon atoms; and R_3 is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R_3 are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R_3 are groups derived from petrolatum, saturated and unsaturated paraffin wax, and the above-described polyalkenes. The groups T, R_2, and R_3 in the above Formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In the above Formulae, a and b are at least 1. In one embodiment, the sulfonic acids have a substituent (R_2 or R_3) which is derived from one of the above-described polyalkenes.

Illustrative examples of these sulfonic acids include monoeicosanyl-substituted naphthalene sulfonic acids, dodecylbenzene sulfonic acids, didodecylbenzene sulfonic acids, dinonylbenzene sulfonic acids, cetylchlorobenzene sulfonic acids, dilauryl beta-naphthalene sulfonic acids, the sulfonic acid derived by the treatment of polybutene having a number average molecular weight (Mn) in the range of 500 to 5000, preferably 800 to 2000, more preferably about 1500 with chlorosulfonic acid, nitronaphthalene sulfonic acid, paraffin wax sulfonic acid, cetyl-cyclopentane, sulfonic acid, lauryl-cyclohexane sulfonic acids, polyethylenyl-substituted sulfonic acids derived from polyethylene (Mn=300-1000, preferably 750), etc. Normally the aliphatic groups will be alkyl and/or alkenyl groups such that the total number of aliphatic carbons is at least about 8, preferably at least 12 up to about 400 carbon atoms, preferably about 250.

Another group of sulfonic acids are mono-, di-, and tri-alkylated benzene and naphthalene (including hydrogenated forms thereof) sulfonic acids. Illustrative of synthetically produced alkylated benzene and naphthalene sulfonic acids are those containing alkyl substituents having from about 8 to about 30 carbon atoms, preferably about 12 to about 30 carbon atoms, and advantageously about 24 carbon atoms. Such acids include di-isododecyl-benzene sulfonic acid, polybutenyl-substituted sulfonic acid, polypropylenyl-substituted sulfonic acids derived from polypropene having an Mn=300-1000, preferably 500-700, cetylchlorobenzene sulfonic acid, di-cetylnaphthalene sulfonic acid, di-lauryldiphenylether sulfonic acid, diisononylbenzene sulfonic acid, di-isooctadecylbenzene sulfonic acid, stearylnaphthalene sulfonic acid, and the like.

Specific examples of oil-soluble sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids;

sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F to about 200 seconds at 210°F; petrolatum sulfonic acids; mono- and poly-wax-substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, etc.; other substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbons), cetylphenol mono-sulfide sulfonic acids, dilauryl beta naphthyl sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids.

Dodecyl benzene "bottoms" sulfonic acids are the material leftover after the removal of dodecyl benzene sulfonic acids that are used for household detergents. These materials are generally alkylated with higher oligomers. The bottoms may be straight-chain or branched-chain alkylates with a straight-chain dialkylate preferred.

The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3, is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

The phosphorus-containing acids useful in making the basic metal salts (A) of the present invention include any phosphorus acids such as phosphoric acid or esters; and thiophosphorus acids or esters, including mono and dithiophosphorus acids or esters. Preferably, the phosphorus acids or esters contain at least one, preferably two, hydrocarbyl groups containing from 1 to about 50 carbon atoms, typically 1 to about 30, preferably 3 to about 18, more preferably about 4 to about 8.

In one embodiment, the phosphorus-containing acids are dithiophosphoric acids which are readily obtainable by the reaction of phosphorus pentasulfide (P_2S_5) and

an alcohol or a phenol. The reaction involves mixing at a temperature of about 20°C to about 200°C four moles of alcohol or a phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated in this reaction. The oxygen-containing analogs of these acids are conveniently prepared by treating the dithioic acid with water or steam which, in effect, replaces one or both of the sulfur atoms with oxygen.

In another embodiment, the phosphorus-containing acid is the reaction product of the above-described polyalkene and phosphorus sulfide. Useful phosphorus sulfide-containing sources include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like.

The reaction of the polyalkene and the phosphorus sulfide generally may occur by simply mixing the two at a temperature above 80°C, preferably between 100°C and 300°C. Generally, the products have a phosphorus content from about 0.05% to about 10%, preferably from about 0.1% to about 5%. The relative proportions of the phosphorizing agent to the olefin polymer is generally from 0.1 part to 50 parts of the phosphorizing agent per 100 parts of the olefin polymer.

The phosphorus-containing acids useful in the present invention are described in U.S. Patent 3,232,883 issued to Le Suer. This reference is herein incorporated by reference for its disclosure to the phosphorus-containing acids and methods for preparing the same.

The phenols useful in making the basic metal salts (A) of the invention can be represented by the formula $(R_1)_a\text{-Ar-}(OH)_b$, wherein R_1 is defined above; Ar is an aromatic group; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. Preferably, a and b are independently numbers in the range of 1 to about 4, more prefera-

bly 1 to about 2. R_1 and a are preferably such that there is an average of at least about 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound.

While the term "phenol" is used herein, it is to be understood that this term is not intended to limit the aromatic group of the phenol to benzene. Accordingly, it is to be understood that the aromatic group as represented by "Ar", as well as elsewhere in other formulae in this specification and in the appended claims, can be mononuclear such as a phenyl, a pyridyl, or a thienyl, or polynuclear. The polynuclear groups can be of the fused type wherein an aromatic nucleus is fused at two points to another nucleus such as found in naphthyl, anthranyl, etc. The polynuclear group can also be of the linked type wherein at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages to each other. These bridging linkages can be chosen from the group consisting of alkylene linkages, ether linkages, keto linkages, sulfide linkages, polysulfide linkages of 2 to about 6 sulfur atoms, etc.

The number of aromatic nuclei, fused, linked or both, in Ar can play a role in determining the integer values of a and b. For example, when Ar contains a single aromatic nucleus, the sum of a and b is from 2 to 6. When Ar contains two aromatic nuclei, the sum of a and b is from 2 to 10. With a tri-nuclear Ar moiety, the sum of a and b is from 2 to 15. The value for the sum of a and b is limited by the fact that it cannot exceed the total number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

The metal compounds useful in making the basic metal salts (A) are generally any Group I or Group II metal compounds (CAS version of the Periodic Table of the Elements). The Group I metals of the metal compound include alkali metals (sodium, potassium, lithium, etc.) as well as

Group IB metals such as copper. The Group I metals are preferably sodium, potassium, lithium and copper, more preferably sodium or potassium, and more preferably sodium. The Group II metals of the metal base include the alkaline earth metals (magnesium, calcium, barium, etc.) as well as the Group IIB metals such as zinc or cadmium. Preferably the Group II metals are magnesium, calcium, or zinc, preferably magnesium or calcium, more preferably magnesium. Generally the metal compounds are delivered as metal salts. The anionic portion of the salt can be hydroxyl, oxide, carbonate, borate, nitrate, etc.

An acidic material is used to accomplish the formation of the basic metal salt (A). The acidic material may be a liquid such as formic acid, acetic acid, nitric acid, sulfuric acid, etc. Acetic acid is particularly useful. Inorganic acidic materials may also be used such as HCl, SO_2, SO_3, CO_2, H_2S, etc, preferably CO_2. A preferred combination of acidic materials is carbon dioxide and acetic acid.

A promoter is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. Among the chemicals useful as promoters are water, ammonium hydroxide, organic acids of up to about 8 carbon atoms, nitric acid, sulfuric acid, hydrochloric acid, metal complexing agents such as alkyl salicylaldoxime, and alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide, and mono- and polyhydric alcohols of up to about 30 carbon atoms. Examples of the alcohols include methanol, ethanol, isopropanol, dodecanol, behenyl alcohol, ethylene glycol, monomethylether of ethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenylethyl alcohol, aminoethanol, cinnamyl alcohol, allyl alcohol, and the like. Especially useful are the monohydric alcohols having up to

about 10 carbon atoms and mixtures of methanol with higher monohydric alcohols.

Patents specifically describing techniques for making basic salts of the above-described sulfonic acids, carboxylic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. The disclosures of these patents are hereby incorporated in this present specification for their disclosures in this regard as well as for their disclosure of specific suitable basic metal salts.

(B) Metal Deactivator

The composition also contains (B) at least one metal deactivator other than a dimercaptothiadiazole or derivatives thereof. Metal deactivators reduce the corrosion of metals, such as copper. Metal deactivators are also referred to as metal passivators. Metal deactivators are typically nitrogen and/or sulfur containing heterocyclic compounds, such as triazoles, amino-mercaptothiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, and derivatives of any one or more thereof. The metal deactivator preferably comprises at least one triazole which may be substituted or unsubstituted. Examples of suitable compounds are benzotriazole, alkyl-substituted benzotriazole (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl-substituted benzotriazole (e.g., phenol benzotriazoles, etc.), and alkylaryl- or arylalkyl-substituted benzotriazole and substituted benzotriazoles where the substituent may be hydroxy, alkoxy, halo (especially chloro), nitro, carboxy and carboxyalkoxy. Preferably, the triazole is a benzotri-

azole or an alkylbenzotriazole in which the alkyl group contains 1 to about 20 carbon atoms, preferably 1 to about 8 carbon atoms. Benzotriazole and tolyltriazole are particularly preferred.

The metal deactivator (B) may also be the reaction product of at least one of the above benzotriazoles with at least one amine. The amine can be one or more mono or polyamines. These monoamines and polyamines can be primary amines, secondary amines or tertiary amines.

The monoamines generally contain from 1 to about 24 carbon atoms, with 1 to about 12 carbon atoms being more preferred, with 1 to about 6 being more preferred. Examples of monoamines useful in the present invention include methylamine, ethylamine, propylamine, butylamine, octylamine, and dodecylamine. Examples of secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, methylbutylamine, ethylhexylamine, etc. Tertiary amines include trimethylamine, tributylamine, methyldiethylamine, ethyldibutylamine, etc.

The polyamines may be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of the polyamines include alkylene polyamines and heterocyclic polyamines.

Alkylene polyamines are represented by the formula

$$\underset{\displaystyle R_4}{\underset{|}{HN}}-(\text{Alkylene}-\underset{\displaystyle R_4}{\underset{|}{N}})_n R_4$$

wherein n has an average value between about 1 and about 10, preferably about 2 to about 7 and the "Alkylene" group has from 1 to about 10 carbon atoms, preferably about 2 to about 6. As noted above, R_4 is preferably an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms.

Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene

polyamines, pentylene polyamines, etc. The higher homologs and related heterocyclic amines such as piperazines and N-amino alkyl-substituted piperazines are also included. Specific examples of such polyamines are ethylene diamine, triethylene tetramine, tris-(2-aminoethyl)amine, propylene diamine, trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylenehexamine, etc..

Higher homologs obtained by condensing two or more of the above-noted alkylene amines are similarly useful as are mixtures of two or more of the aforedescribed polyamines.

Ethylene polyamines, such as some of those mentioned above, are useful. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Such polyamines are most conveniently prepared by the reaction of ethylene dichloride with ammonia or by reaction of an ethylene imine with a ring opening reagent such as water, ammonia, etc. These reactions result in the production of a complex mixture of polyalkylene polyamines including cyclic condensation products such as piperazines. Ethylene polyamine mixtures are useful.

The amine may also be a heterocyclic polyamine. Among the heterocyclic polyamines are aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the satu-

rated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkylsubstituted piperidines, piperazine, aminoalkyl-substituted piperazines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N′-diaminoethylpiperazine.

Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave as residue what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than two, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably DETA), 0.72% TETA, 21.74% tetraethylene pentamine and 76.61% pentaethylene hexamine and higher (by weight). These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like.

These alkylene polyamine bottoms can be reacted solely with the acylating agent, in which case the amino reactant consists essentially of alkylene polyamine bottoms, or they can be used with other amines, polyamines, or mixtures thereof.

Amines useful in the present invention are described in U.S. Patents 3,219,666 and 4,234,435, and these patents are hereby incorporated by reference for their disclosures of amines.

Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols and amines. The polyhydric alcohols contain from 2 to about 10, preferably 2 to about 6, preferably 2 to about 4 hydroxyl groups and up to 40 aliphatic carbon atoms, preferably from 2 to about 30, more preferably 2 to about 10. The polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and penterythritols, including di- and tripentaerythritol. Preferably the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having two to about 20 carbon atoms, preferably two to about four. Examples of polyhydric amines include tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine, and N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine,preferably tris(hydroxymethyl)aminomethane (THAM).

Polyamine reactants, which react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamine reactants include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine

(PEHA), and mixtures of polyamines such as the above-described "amine bottoms".

The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually about 60°C to about 265°C, (preferably about 220°C to about 250°C) in the presence of an acid catalyst.

The amine condensates and methods of making the same are described in PCT publication WO86/05501 which is incorporated by reference for its disclosure to the condensates and methods of making. The preparation of such polyamine condensates may occur as follows: A 4-necked 3-liter round-bottomed flask equipped with glass stirrer, thermowell, subsurface N_2 inlet, Dean-Stark trap, and Friedrich condenser is charged with: 1299 grams of HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1% by weight nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), and 727 grams of 40% aqueous tris(hydroxymethyl)aminomethane (THAM). This mixture is heated to 60°C and 23 grams of 85% H_3PO_4 is added. The mixture is then heated to 120°C over 0.6 hour. With N_2 sweeping, the mixture is then heated to 150°C over 1.25 hour, then to 235°C over 1 hour more, then held at 230-235°C for 5 hours, then heated to 240°C over 0.75 hour, and then held at 240-245°C for 5 hours. The product is cooled to 150°C and filtered with a diatomaceous earth filter aid. Yield: 84% (1221 grams).

The metal deactivator may also be the reaction product of one or more of the above triazoles and at least one compound selected from acylated nitrogen compounds, hydrocarbyl substituted amines and Mannich reaction products.

The acylated nitrogen compounds include reaction products of amines, hydrocarbyl-substituted carboxylic acylating agents such as substituted carboxylic acids or derivatives thereof. The amines are described above, typically the amines are polyamines, preferably the amines are ethylene amines, amine bottoms or amine condensates.

The hydrogen-substituted carboxylic acylating agent may be derived from a monocarboxylic acid or a polycarboxylic acid. Polycarboxylic acids generally are preferred. The acylating agents may be a carboxylic acid or derivatives of the carboxylic acid such as the halides, esters, anhydrides, etc., preferably acid, esters or anhydrides, more preferably anhydrides. Preferably the carboxylic acylating agent is a succinic acylating agent.

The hydrocarbyl-substituted carboxylic acylating agent includes agents which have a hydrocarbyl group derived from the above-described polyalkenes.

In another embodiment, the hydrocarbyl groups are derived from polyalkenes having an Mn value of at least about 1300 up to about 5000, and the Mw/Mn value is from about 1.5 to about 4, preferably from about 1.8 to about 3.6, more preferably about 2.5 to about 3.2. The preparation and use of substituted succinic acylating agents wherein the substituent is derived from such polyolefins are described in U.S. Patent 4,234,435, the disclosure of which is hereby incorporated by reference.

The hydrocarbyl-substituted carboxylic acylating agents are prepared by a reaction of one or more polyalkenes with one or more unsaturated carboxylic reagent. The unsaturated carboxylic reagent generally contains an alpha-beta olefinic unsaturation. The carboxylic reagents may be carboxylic acids per se and functional derivatives thereof, such as anhydrides, esters, amides, imides, salts, acyl halides, and nitriles. These carboxylic acid reagents may be either monobasic or polybasic in nature. When they

are polybasic they are preferably dicarboxylic acids, although tri- and tetracarboxylic acids can be used. Specific examples of useful monobasic unsaturated carboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 2-phenylpropenoic acid, etc. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid. Generally, the unsaturated carboxylic acid or derivative is maleic anhydride or maleic or fumaric acid or ester, preferably, maleic acid or anhydride, more preferably maleic anhydride.

The polyalkene may be reacted with the carboxylic reagent such that there is at least one mole of reagent for each mole of polyalkene. Preferably, an excess of reagent is used. This excess is generally between about 5% to about 25%.

In another embodiment, the acylating agents are prepared by reacting the above described polyalkene with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group is at least 1.3. The maximum number will not exceed 4.5. A suitable range is from about 1.4 to 3.5 and more specifically from about 1.4 to about 2.5 succinic groups per equivalent weight of substituent groups. In this embodiment, the polyalkene preferably has an Mn from about 1300 to about 5000 and a Mw/Mn of at least 1.5, as described above, the value of Mn is preferably between about 1300 and 5000. A more preferred range for Mn is from about 1500 to about 2800, and a most preferred range of Mn values is from about 1500 to about 2400.

The conditions, i.e., temperature, agitation, solvents, and the like, for reacting an acid reactant with a polyalkene, are known to those in the art. Examples of patents describing various procedures for preparing useful acylating agents include U.S. Patents 3,215,707 (Rense);

3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219. The disclosures of these patents are hereby incorporated by reference.

The hydrocarbyl-substituted amines, which may be reacted with a triazole, are well known to those skilled in the art. These amines are disclosed in U.S. patents 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433; and 3,822,289. These patents are hereby incorporated by reference for their disclosure of hydrocarbyl amines and methods of making the same.

Typically, hydrocarbyl-substituted amines are prepared by reacting olefins and olefin polymers (polyalkenes) with amines (mono- or polyamines). The polyalkene may be any of the polyalkenes described above. The amines may be any of the amines described above. Examples of these substituted amines include poly(propylene)amine; N,N-dimethyl-N-poly(ethylene/propylene)amine, (50:50 mole ratio of monomers); polybutene amine; N,N-di(hydroxyethyl)-N-polybutene amine; N-(2-hydroxypropyl)-N-polybutene amine; N-polybutene-aniline; N-polybutenemorpholine; N-poly(butene)ethylenediamine; N-poly(propylene)trimethylenediamine; N-poly(butene)diethylenetriamine; N′,N′-poly(butene)tetraethylenepentamine; N,N-dimethyl-N′-poly(propylene)-1,3-propylenediamine and the like.

The triazole may also be reacted with a Mannich reaction product. Mannich reaction products are formed by the reaction of at least one aldehyde, at least one of the above described amine and at least one hydroxyaromatic compound. The reaction may occur from room temperature to 225°C, usually from 50° to about 200°C (75°C-125°C most preferred), with the amounts of the reagents being such that the molar ratio of hydroxyaromatic compound to formaldehyde to amine is in the range from about (1:1:1) to about (1:3:3).

The first reagent is a hydroxyaromatic compound. This term includes phenols (which are preferred), carbon-, oxygen-, sulfur- and nitrogen-bridged phenols and the like as well as phenols directly linked through covalent bonds (e.g. 4,4'-bis(hydroxy)biphenyl), hydroxy compounds derived from fused-ring hydrocarbon (e.g., naphthols and the like); and polyhydroxy compounds such as catechol, resorcinol and hydroquinone. The hydroxyaromatic compound may be any of the above-described phenols. Mixtures of one or more hydroxyaromatic compounds can be used as the first reagent.

The hydroxyaromatic compound is preferably one of the above-described phenols. In one embodiment, the hydroxyaromatic compound is phenol substituted with an aliphatic or alicyclic hydrocarbon-based group having an Mn of about 420 to about 10,000.

The second reagent is a hydrocarbon-based aldehyde, preferably a lower aliphatic aldehyde. Suitable aldehydes include formaldehyde, benzaldehyde, acetaldehyde, the butyraldehydes, hydroxybutyraldehydes and heptanals, as well as aldehyde precursors which react as aldehydes under the conditions of the reaction such as paraformaldehyde, paraldehyde, formalin and methanal. Formaldehyde and its precursors (e.g., paraformaldehyde, trioxane) are preferred. Mixtures of aldehydes may be used as the second reagent.

The third reagent is any amine described above. Preferably the amine is a polyamine as described above.

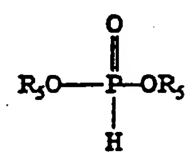
Mannich reaction products are described in the following patents: U.S. Patent 3,980,569; U.S. Patent 3,877,899; and U.S. Patent 4,454,059 (herein incorporated by reference for their disclosure to Mannich reaction products, also referred to as Mannich dispersants).

The triazole-amine, -acylated amine, -hydrocarbyl substituted amine and -Mannich reaction products may be prepared by blending the reagents and allowing the reaction

to proceed. The reaction may occur at a temperature as low as about 15°C, up to about 160°C, with temperatures in the range of about 60°C to about 140°C being preferred. The triazole-amine, -acylated nitrogen compound, -hydrocarbyl substituted amine and -Mannich reaction products may be reacted in any proportion but are preferably reacted at an equal equivalent ratio.

<u>(C) Hydrocarbyl Phosphites</u>

Compositions of the present invention also include (C) a hydrocarbyl phosphite. The phosphite may be represented by the following formulae:



or

$$(R_5O)_3P$$

wherein each R_5 is independently hydrogen or a hydrocarbyl group, provided at least one R_5 is hydrocarbyl.

Preferably each R_5 is independently a hydrogen or hydrocarbyl group having from 1 to about 24, more preferably from 1 to about 18, and more preferably from about 2 to about 8 carbon atoms. Each R_5 may be independently alkyl, alkenyl or aryl. When R_5 is aryl it contains at least 6 carbon atoms; preferably 6 to about 18 carbon atoms. Examples of alkyl or alkenyl groups are propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, etc. Examples of aryl groups are phenyl, napthyl, heptylphenol, etc. Preferably each R_5 is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl or phenyl, more preferably butyl, oleyl or phenyl and more preferably butyl or oleyl.

The R_5 groups may also comprise a mixture of hydrocarbyl groups derived from commercial alcohols.

Examples of preferred monohydric alcohols and alcohol mixtures include commercially available "Alfol" alcohols marketed by Continental Oil Corporation. Alfol 810 is a mixture containing alcohols consisting essentially of straight-chain, primary alcohols having 8 to 10 carbon atoms. Alfol 812 is a mixture comprising mostly C_{12} fatty alcohols. Alfol 1218 is a mixture of synthetic, primary, straight-chain alcohols having from 12 to 18 carbon atoms. Alfol 20+ alcohols are mixtures of 18-28 primary alcohols having mostly, on an alcohol basis, C_{20} alcohols as determined by GLC (gas-liquid-chromatography).

Another group of commercially available alcohol mixtures includes the "Neodol" products available from Shell Chemical Company. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} and C_{15} linear alcohols. Neodol 91 is a mixture of C_9, C_{10} and C_{11} alcohols.

Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutylhydrogen phosphite, trioleyl phosphite and triphenyl phosphite. Phosphite esters are generally dialkyl hydrogen phosphites.

A number of dialkyl hydrogen phosphites are commercially available, such as lower dialkyl hydrogen phosphites, which are preferred. Lower dialkyl hydrogen phosphites include dimethyl, diethyl, dipropyl, dibutyl, dipentyl and dihexyl hydrogen phosphites. Also mixed alkyl hydrogen phosphites are useful in the present invention. Examples of mixed alkyl hydrogen phosphites include ethyl, butyl; propyl, pentyl; and methyl, pentyl hydrogen phosphites.

(D) Sulfur-, Phosphorus-, or Sulfur- and Phosphorus-Containing Antiwear Agents

Although not required, the composition of the present invention may include a supplemental sulfur-, phosphorus-, or sulfur- and phosphorus-containing antiwear agent. The term antiwear agent is used in the specification and claims to refer to compounds which provide wear protection properties to lubricating compositions and functional fluids. The antiwear agent is useful in controlling wear and may also act as an extreme pressure agent. These antiwear agents include (D-1) sulfurized organic compounds, (D-2) hydrocarbyl phosphates, (D-3) phosphorus-containing amides, (D-4) phosphorus-containing carboxylic esters, (D-5) phosphorus-containing ethers, and (D-6) dithiocarbamate-containing compounds. Of course, the above antiwear agents may provide other useful properties, such as friction modification.

(D-1) Sulfurized Organic Compositions

In one embodiment, the antiwear agent (D) is a sulfurized organic composition (D-1), preferably a sulfurized olefin, more preferably a mono-, or disulfide or mixtures thereof. The sulfurized organic compounds useful in the present invention are generally characterized as having sulfide linkages having from about 1 to about 10 sulfur atoms, preferably about 1 to about 4, more preferably about 1 or about 2.

Materials which may be sulfurized to form the sulfurized organic compositions of the present invention include oils, fatty acids or esters, olefins or polyolefins made thereof, turpenes, or Diels-Alder adducts.

Oils which may be sulfurized are natural or synthetic oils including mineral oils, lard oil, carboxylic acid esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and

oleyl oleate) sperm whale oil and synthetic sperm whale oil substitutes and synthetic unsaturated esters or glycerides.

Fatty acids generally contain from about 4 to about 22 carbon atoms. The unsaturated fatty acids generally contained in the naturally occurring vegetable or animal fats and oils may contain one or more double bonds and such acids include palmitoleic acid, oleic acid, linoleic acid, linolenic acid, and erucic acid. The unsaturated fatty acids may comprise mixtures of acids such as those obtained from naturally occurring animal and vegetable oils such as lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil, or wheat germ oil. Tall oil is a mixture of rosin acids, mainly abietic acid, and unsaturated fatty acids, mainly oleic and linoleic acids. Tall oil is a by-product of the sulfate process for the manufacture of wood pulp.

The most particularly preferred unsaturated fatty acid esters useful in this invention are the fatty oils, that is, naturally occurring esters of glycerol with the fatty acids described above, and synthetic esters of similar structure. Examples of naturally occurring fats and oils containing unsaturation include animal fats such as Neat's-foot oil, lard oil, depot fat, beef tallow, etc. Examples of naturally occurring vegetable oils include cottonseed oil, corn oil, poppy-seed oil, safflower oil, sesame oil, soybean oil, sunflower seed oil and wheat germ oil.

The fatty acid esters also may be prepared from aliphatic olefinic acids of the type described above such as oleic acid, linoleic acid, linolenic acid, and behenic acid by reaction with alcohols and polyols. Examples of aliphatic alcohols which may be reacted with the above-identified acids include monohydric alcohols such as methanol, ethanol, n-propanol, isopropanol, the butanols, etc.; and polyhydric alcohols including ethylene glycol,

propylene glycol, trimethylene glycol, neopentyl glycol, glycerol, etc.

The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula $R^{*1}R^{*2}C{=}CR^{*3}R^{*4}$, wherein each of R^{*1}, R^{*2}, R^{*3} and R^{*4} is hydrogen or an organic group. In general, the R^{*} groups in the above formula which are not hydrogen may be satisfied by such groups as $-C(R^{*5})_3$, $-COOR^{*5}$, $-CON(R^{*5})_2$, $-COON(R^{*5})_4$, -COOM, -CN, -X, $-YR^{*5}$ or -Ar, wherein:

each R^{*5} is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^{*5} groups can be alkylene or substituted alkylene whereby a ring of up to about 12 carbon atoms is formed;

M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium);

X is halogen (e.g., chloro, bromo, or iodo);

Y is oxygen or divalent sulfur;

Ar is an aryl or substituted aryl group of up to about 12 carbon atoms.

Any two of R^{*1}, R^{*2}, R^{*3} and R^{*4} may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

The olefinic compound is usually one in which each R group which is not hydrogen is independently alkyl, alkenyl or aryl group. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^{*3} and R^{*4} are hydrogen and R^{*1} and R^{*2} are alkyl or aryl, especially alkyl (that is, the olefin is aliphatic) having 1 to about 30, preferably 1 to about 16, more preferably 1 to about 8, and more preferably 1 to

about 4 carbon atoms. Olefinic compounds having about 3 to 30 and especially about 3 to 16 (most often less than 9) carbon atoms are particularly desirable.

Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutylene and diisobutylene are particularly desirable because of their availability and the particularly high sulfurcontaining compositions which can be prepared therefrom.

In another embodiment, the sulfurized organic compound (D-1) is a sulfurized terpene compound. The term "terpene compound" as used in the specification and claims is intended to include the various isomeric terpene hydrocarbons having the empirical formula $C_{10}H_{16}$, such as contained in turpentine, pine oil and dipentenes, and the various synthetic and naturally occuring oxygen-containing derivatives. Mixtures of these various compounds generally will be utilized, especially when natural products such as pine oil and turpentine are used. Pine oil, for example, which is obtained by destructive distillation of waste pine wood with super-heated steam comprises a mixture of terpene derivatives such as alpha-terpineol, beta-terpineol, alpha-fenchol, camphor, borneol/isoborneol, fenchone, estragole, dihydro alpha-terpineol, anethole, and other mono-terpene hydrocarbons. The specific ratios and amounts of the various components in a given pine oil will depend upon the particular source and the degree of purification. A group of pine oil-derived products are available commercially from Hercules Incorporated. It has been found that the pine oil products generally known as terpene alcohols available from Hercules Incorporated are particularly useful in the preparation of the sulfurized products of the invention. Examples of such products include alpha-Terpineol containing about 95-97% of alpha-terpineol, a high purity tertiary terpene alcohol mixture typically contain-

ing 96.3% of tertiary alcohols; Terpineol 318 Prime which is a mixture of isomeric terpineols obtained by dehydration of terpene hydrate and contains about 60-65 weight percent of alpha-terpineol and 15-20% beta-terpineol, and 18-20% of other tertiary terpene alcohols. Other mixtures and grades of useful pine oil products also are available from Hercules under such designations as Yarmor 302, Herco pine oil, Yarmor 302W, Yarmor F and Yarmor 60.

In one embodiment, sulfurized olefins are produced by (1) reacting sulfur monochloride with a stoichiometric excess of a low carbon atom olefin, (2) treating the resulting product with an alkali metal sulfide in the presence of free sulfur in a mole ratio of no less than 2:1 in an alcohol-water solvent, and (3) reacting that product with an inorganic base. This procedure is described in U.S. Patent 3,471,404, and the disclosure of U.S. Patent 3,471,404 is hereby incorporated by reference for its discussion of this procedure for preparing sulfurized olefins and the sulfurized olefins thus produced. Generally, the olefin reactant contains from about 2 to 5 carbon atoms and examples include ethylene, propylene, butylene, isobutylene, amylene, etc.

The sulfurized olefins which are useful in the compositions of the present invention also may be prepared by the reaction, under superatmospheric pressure, of olefinic compounds with a mixture of sulfur and hydrogen sulfide in the presence of a catalyst, followed by removal of low boiling materials. This procedure for preparing sulfurized compositions which are useful in the present invention is described in U.S. Patent 4,191,659, the disclosure of which is hereby incorporated by reference for its description of the preparation of useful sulfurized compositions.

In another embodiment, the sulfurized organic composition (D-1) is at least one sulfur-containing materi-

al which comprises the reaction product of a sulfur source and at least one Diels-Alder adduct in a molar ratio of at least 0.75:1. Generally, the molar ratio of sulfur source to Diels-Alder adduct is in a range of from about 0.75 to about 4.0, preferably about 1 to about 2.0, more preferably about 1 to about 1.8. In one embodiment the molar ratio of sulfur to adduct is from about 0.8:1 to 1.2:1.

The Diels-Alder adducts are a well-known, art-recognized class of compounds prepared by the diene synthesis or Diels-Alder reaction. A summary of the prior art relating to this class of compounds is found in the Russian monograph, Dienovyi Sintes, Izdatelstwo Akademii Nauk SSSR, 1963 by A.S. Onischenko. (Translated into the English language by L. Mandel as A.S. Onischenko, Diene Synthesis, N.Y., Daniel Davey and Co., Inc., 1964.) This monograph and references cited therein are incorporated by reference into the present specification.

Basically, the diene synthesis (Diels-Alder reaction) involves the reaction of at least one conjugated diene with at least one ethylenically or acetylenically unsaturated compound, these latter compounds being known as dienophiles. Piperylene, isoprene, methylisoprene, chloroprene, and 1,3-butadiene are among the preferred dienes for use in preparing the Diels-Alder adducts.

In addition to these linear 1,3-conjugated dienes, cyclic dienes are also useful as reactants in the formation of the Diels-Alder adducts. Examples of these cyclic dienes are the cyclopentadienes, fulvenes, 1,3-cyclohexadienes, 1,3-cycloheptadienes, 1,3,5-cycloeptatrienes, cyclooctatetraene, and 1,3,5-cyclononatrienes. Various substituted derivatives of these compounds enter into the diene synthesis.

Dienophiles, useful in preparing the Diels-Alder adducts, include those having at least one electron-accepting groups selected from groups such as formyl, cyano,

nitro, carboxy, carbohydrocarbyloxy, hydrocarbyl- carbonyl, hydrocarbylsulfonyl, carbamyl, acylcarbamyl, N-acyl-N-hydrocarbylcarbamyl, N-hydrocarbylcarbamyl, and N,N-dihydrocarbylcarbamyl. The dienophiles include: nitroalkenes; alpha,beta-ethylenically unsaturated carboxylic esters, acids or amides; ethylenically unsaturated aldehydes and vinyl ketones. Specific examples of dienophiles include 1-nitrobutene-1, alkylacrylates, acrylamide, dibutylacrylamide, methacrylamide, crotonaldehyde; crotonic acid, dimethyldivinyl ketone, methylvinyl ketone and the like.

Another class of dienophiles are those having at least one carboxylic ester group represented by $-C(O)O-R_0$ where R_0 is the residue of a saturated aliphatic alcohol of up to about 40 carbon atoms, the aliphatic alcohol from which $-R_0$ is derived can be a mono or polyhydric alcohol such as alkyleneglycols, alkanols, aminoalkanols, alkoxy-substituted alkanols, ethanol, ethoxy ethanol, propanol, beta-diethylamino-ethanol, dodecyl alcohol, diethylene glycol, tripropylene glycol, tetrabutylene glycol, hexanol, octanol, isooctyl alcohol, and the like. In this especially preferred class of dienophiles, not more than two $-C(O)-O-R_0$ groups will be present, preferably only one $-C(O)-O-R_0$ group.

In addition to the ethylenically unsaturated dienophiles, there are many useful acetylenically unsaturated dienophiles such as propiolaldehyde, methyl-ethynylketone, propylethynylketone, propenylethynylketone, propiolic acid, propiolic acid nitrile, ethyl-propiolate, tetrolic acid, propargylaldehyde, acetylene-dicarboxylic acid, the dimethyl ester of acetylenedicarboxylic acid, dibenzoylacetylene, and the like.

Cyclic dienophiles include cyclopentenedione, coumarin, 3-cyanocoumarin, dimethyl maleic anhydride, 3,6-endomethylene-cyclohexenedicarboxylic acid, etc. With the exception of the unsaturated dicarboxylic anhydrides

derived from linear dicarboxylic acids (e.g., maleic anhydride, methylmaleic anhydride, chloromaleic anhydride), this class of cyclic dienophiles are limited in commercial usefulness due to their limited availability and other economic considerations.

Normally, the adducts involve the reaction of equimolar amounts of diene and dienophile. However, if the dienophile has more than one ethylenic linkage, it is possible for additional diene to react if present in the reaction mixture.

The sulfur-containing Diels-Alder adducts are readily prepared by heating a mixture of a sulfur source, preferably sulfur and at least one of the Diels-Alder adducts of the types discussed hereinabove at a temperature within the range of from about 110°C to just below the decomposition temperature of the Diels-Alder adducts. Temperatures within the range of about 110° to about 200°C will normally be used.

The reaction can be conducted in the presence of suitable inert organic solvents such as mineral oils, alkanes of 7 to 18 carbons, etc., although no solvent is generally necessary. After completion of the reaction, the reaction mass can be filtered and/or subjected to other conventional purification techniques.

The following examples illustrate the preparation of the sulfurized organic compound (D-1) useful in the present invention. Unless otherwise indicated, in the following examples as well as elsewhere in the specification and claims, temperature is in degrees Celsius, parts and percentages are by weight and pressures are atmospheric.

EXAMPLE 1

A reaction mixture comprising 1175 parts (6 moles) of the Diels-Alder adduct of butyl acrylate and isoprene, and 384 parts (12 moles) of sulfur flowers is

heated for 0.5 hour at 108-110°C, and then to 155-165°C for 6 hours while bubbling nitrogen gas through the reaction mixture at 0.25 to 0.5 SCFH. At the end of this heating period the reaction mixture is allowed to cool and is filtered at room temperature. The product is allowed to stand at room temperature for one day and is then refiltered. The filtrate which is the desired product weighs 1278 parts.

EXAMPLE 2

A mixture of 910 parts (5 moles) of a butyl acrylate-butadiene adduct prepared as in Example 7, 128 parts (4 moles) of sulfur and 9 parts of triphenyl phosphite is prepared and heated with stirring while sweeping with nitrogen to a temperature of 142°C over a period of about one hour. The heating is continued to raise the temperature to 185-186°C over about 2 hours and the mixture is maintained at 185-187°C for 3.2 hours. After allowing the reaction mixture to cool to 96°C, the mixture is filtered with filter aid, and the filtrate is the desired product containing 12.0% sulfur.

EXAMPLE 3

The general procedure of Example 2 is repeated except that the mixture contain 259 parts (8.09 mole) of sulfur. The product obtained in this manner contains 21.7% sulfur.

EXAMPLE 4

Sulfur (526 parts, 16.4 moles) is charged to a jacketed, high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 2 torr and cooling, 920 parts (16.4 moles) of isobutene and 279 parts (8.2 moles) of hydrogen sulfide are charged to the reactor. The reactor is heated using steam in the external jacket, to a

temperature of about 182°C over about 1.5 hours. A maximum pressure of 1350 psig is reached at about 168°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 10 hours at a reaction temperature of about 182°C, the pressure is 310-340 psig and the rate of pressure change is about 5-10 psig per hour. The unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid.

The mixture is blown with nitrogen at about 100°C to remove low boiling materials including unreacted isobutene, mercaptans and monosulfides. The residue after nitrogen blowing is agitated with 5% Super Filtrol and filtered, using a diatomaceous earth filter aid. The filtrate is the desired sulfurized composition which contains 42.5% sulfur.

EXAMPLE 5

Sulfur monochloride (2025 parts, 15.0 moles) is heated to 45°C. Through a sub-surface gas sparger, 1468 parts (26.2 moles) of isobutylene gas are fed into the reactor over a 5-hour period. The temperature is maintained between 45-50°C. At the end of the sparging, the reaction mixture increases in weight of 1352 parts.

In a separate reaction vessel are added 2150 parts (16.5 moles) of 60% flake sodium sulfide, 240 parts (7.5 moles) sulfur, and a solution of 420 ml. of isopropanol in 4000 ml. of water. The contents are heated to 40°C. The adduct of the sulfur monochloride and isobutylene previously prepared is added over a three-quarter hour period while permitting the temperature to rise to 75°C. The reaction mixture is refluxed for 6 hours, and afterward the mixture is permitted to form into separate layers. The lower aqueous layer is discarded. The upper organic layer

is mixed with two liters of 10% aqueous sodium hydroxide, and the mixture is refluxed for 6 hours. The organic layer is again removed and washed with one liter of water. The washed product is dried by heating at 90°C and 30 mm. Hg. pressure for 30 minutes. The residue is filtered through diatomaceous earth filter aid to give 2070 parts of a clear yellow-orange liquid.

EXAMPLE 6

A mixture of 100 parts of soybean oil and 50 parts of commercial C_{16} α-olefins is heated to 175°C. under nitrogen and 17.4 parts of sulfur is added gradually, whereupon an exothermic reaction causes the temperature to rise to 205°C. The mixture is heated at 188°-200°C. for 5 hours, allowed to cool gradually to 90°C. and filtered to yield the desired product containing 10.13% sulfur.

EXAMPLE 7

A mixture of 100 parts of soybean oil, 3.7 parts of tall oil acid and 46.3 parts of commercial C_{15-18} α-olefins is heated to 165°C. under nitrogen and 17.4 parts of sulfur is added. The temperature of the mixture rises to 191°C. It is maintained at 165°-200°C. for 7 hours and is then cooled to 90°C. and filtered. The product contains 10.13% sulfur.

(D-2) Hydrocarbyl Phosphate

In one embodiment, the antiwear agent (D) is a hydrocarbyl phosphate (D-2). The phosphate may be a mono-, di- or trihydrocarbyl phosphate. The hydrocarbyl groups each independently contain from 1 to about 30 carbon atoms, preferably 1 to about 24 carbon atoms, more preferably 1 to about 12 carbon atoms. In a preferred embodiment, each hydrocarbyl is independently an alkyl or aryl group. When any group is an aryl group it contains from 6 to about 24 carbon atoms, more preferably 6 to about 18 carbon atoms. Examples of hydrocarbyl groups include a butyl, amyl,

hexyl, octyl, oleyl or cresyl, with octyl and cresyl being preferred.

The hydrocarbyl phosphates (D-2) of the present invention may be prepared by reacting phosphorus acid or anhydride, preferably phosphorus pentaoxide with an alcohol at a temperature of about 30°C to about 200°C, preferably 80°C to about 150°C. The phosphorus acid is generally reacted with the alcohol in a ratio of about 1:3.5, preferably 1:3.

The hydrocarbyl groups may be derived from a mixture of hydrocarbyl groups derived from the above-described commercial alcohols (see phosphite). Also useful hydrocarbyl groups derived from Alfol 22+ alcohols are C_{18}-C_{28} primary alcohols having mostly, on an alcohol basis, C_{22} alcohols. These Alfol alcohols can contain a fairly large percentage (up to 40% by weight) of paraffinic compounds which can be removed before the reaction if desired.

Another example of a commercially available alcohol mixture is Adol 60 which comprises about 75% by weight of a straight chain C_{22} primary alcohol, about 15% of a C_{20} primary alcohol and about 8% of C_{18} and C_{24} alcohols. Adol 320 comprises predominantly oleyl alcohol. The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length of from C_8 to C_{18} are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C_{10} alcohol, 66.0% of C_{12} alcohol, 26.0% of C_{14} alcohol and 6.5% of C_{16} alcohol. Another group of commercially available mixtures include the above-described "Neodol" products available from Shell Chemical Co.

Fatty vicinal diols also are useful and these include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha olefin fraction of C_{11}-C_{14}, and the latter is derived from a C_{15}-C_{18} fraction.

In another embodiment, the hydrocarbyl phosphate (D-2) may be a hydrocarbyl thiophosphate. Thiophosphates may contain from one to about three sulfur atoms, preferably one or two sulfur atoms. The thiophosphates may have the same hydrocarbyl group as described above. Thiophosphates are prepared by reacting one or more of the above-described phosphites with a sulfurizing agent including sulfur, sulfur halides, and sulfur containing compounds, such as sulfurized olefins, sulfurized fats, mercaptans and the like.

The following example relates to preparation of thiophosphates.

EXAMPLE 8

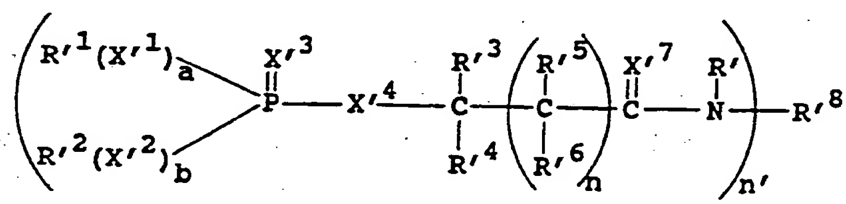
A reaction vessel is charged with 1204 parts (3.69 equivalents) of triphenylphosphite. The phosphite is heated to 160°C. where 112 parts (3.51 equivalents) of sulfur is added over three hours. The reaction temperature is maintained at 160°C. for four hours. The mixture is filtered through diatomaceous earth and the filtrate is the desired product. The filtrate contains 8.40% phosphorous (8.7% theory) and 8.4% sulfur (8.50% theory).

(D-3) Phosphorus-Containing Amides

In another embodiment, the antiwear agent (D) may be a phosphorus-containing amide (D-3). Phosphorus-containing amides are generally prepared by reacting one of the above-described phosphorus acids such as a phosphoric, phosphonic, phosphinic, thiophosphoric, including dithiophosphoric as well as monothiophosphoric, thiophosphinic or thiophosphonic acids with an unsaturated amide, such as an acrylamide. Preferably the phosphorus acid is a dithio-

phosphorus acid prepared by reacting a phosphorus sulfide with an alcohol or phenol to form dihydrocarbyl dithiophosphoric acid. The hydrocarbyl groups may be those described above for hydrocarbyl phosphates.

In one embodiment, the antiwear agent (D) is a phosphorus-containing amide (D-3) represented by the formula:



wherein each X'^1, X'^2, X'^3, X'^4 and X'^5 is independently oxygen or sulfur;

each R'^1 and R'^2 is independently a hydrocarbyl group;

each R'^3, R'^4, R'^5, R'^6 and R'^7 is independently a hydrogen, halogen or hydrocarbyl group;

a and b independently are zero or 1;

n is zero or 1;

n' is 1, 2 or 3;

with the proviso that:

(1) when n' is 1, R'^8 is hydrogen, -R', -ROH, -ROR, -RSR or

$$-R'-\overset{\displaystyle R'}{\overset{|}{N}}-R' ;$$

(2) when n' is 2, R'^8 is a coupling group selected from -R'-, -R*-, -R'-O-R'-, -R'-S-R'-,

$$-R'-\overset{\displaystyle O}{\overset{\|}{C}}-R'-,\ -R'-\overset{\displaystyle S}{\overset{\|}{C}}-R'-,\ -R'-\overset{\displaystyle H}{\overset{|}{N}}-R'-\ \text{or}\ -R'-\overset{\displaystyle R'}{\overset{|}{N}}-R'- ;\ \text{and}$$

(3) when n' is 3, R'^8 is the coupling group

$$-R'-\underset{\underset{\displaystyle |}{\displaystyle R'}}{\underset{|}{N}}-R'-$$

wherein each R' is independently a hydrocarbyl group of 1 to about 12 carbon atoms; and each R' is independently an arylene, or an alkylene or alkylidene group having from 1 to about 12 carbon atoms.

X'^1, X'^2 and X'^5 are preferably oxygen. X'^3 and X'^4 are preferably sulfur and a and b are preferably 1.

Each R'^1 and R'^2 is independently a hydrocarbyl group of from 1 to about 50 carbon atoms, more preferably from 1 to about 30 carbon atoms, more preferably from about 3 to about 18 carbon atoms, more preferably from about 4 to about 8 carbon atoms. Each R'^1 and R'^2 is preferably an alkyl group. Examples of R'^1 and R'^2 are independently t-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphtyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylnaphthylalkyl groups, and the like.

Each R'^3, R'^4, R'^5, R'^6 and R'^7 is independently a hydrogen or hydrocarbyl group of 1 from about 50 carbon atoms, more preferably 1 to about 30, more preferably 1 to about 18, more preferably 1 to about 8. Advantageously, each R'^3, R'^4, R'^5, R'^6 and R'^7 is independently a hydrogen; an alkyl group of from 1 to about 22 carbon atoms; a cyclo-alkyl group of from about 4 to about 22 carbon atoms; or an aromatic, an alkyl-substituted aromatic or an aromatic-substituted alkyl group of from about 4 to about 34 carbon atoms.

Preferably each R' is independently an alkylene or alkylidene group having from 1 to about 12, more preferably from 1 to about 6, more preferably 1 carbon atom. R' is preferably methylene, ethylene, or propylene with preferably methylene.

The phosphorus-containing amides (D-3) may be prepared by the reaction of a phosphorus-containing acid, preferably a dithiophosphoric acid, as described above with an acrylamide such as acrylamide, N,N'-methylenebisacryl-

amide, methacrylamide, crotonamide, and the like. The reaction product from above may be further reacted with linking or coupling compounds, such as formaldehyde or paraformaldehyde to form coupled compounds.

The phosphorus-containing amides are known in the art and are disclosed in U.S. Patents 4,876,374, 4,770,807 and 4,670,169 which are incorporated by reference for its disclosure of the phosphorus amides, and their preparation.

The following examples illustrate the phosphorus containing amides (D-3) of the present invention.

EXAMPLE 9

To 1017 parts (3.0 equivalents) of O,O-di-4-methyl-2-pentyl phosphorodithioic acid under nitrogen is added 213 parts (3.0 equivalents) of acrylamide. The reaction exotherms to 65°C. and is held for one to three hours at 65°-75°C. The product is filtered through diatomaceous earth and the filtrate is the desired product. The product contains 7.65% phosphorus (7.82% theory), 3.51% nitrogen (3.50% theory), and 16.05% sulfur (16.06% theory).

EXAMPLE 10

To a mixture of 1494 parts (3.79 equivalents) of O,O-di-isooctyl phosphorodithioic acid and 800 parts of toluene under a nitrogen atmosphere are added 537 parts (3.79) equivalents of 50% aqueous acrylamide solution over a period of one hour. The reaction mixture exotherms to about 53°C. and 64 parts (1.93 equivalents) of paraformaldehyde and 18 parts (0.095 equivalent) of p-toluenesulfonic hydrate are added. Heating is continued at reflux (91°-126°C.) for four hours while collecting 305 parts of water. The mixture is cooled to about 90°C. and 7.6 parts (0.095 equivalent) of 50% aqueous sodium hydroxide solution are added. Cooling is continued to about 30°C. and a vacuum is applied (15 mm. Hg). Toluene solvent is removed while raising the temperature to 110°C. The residue is filtered through diatomaceous earth and the filtrate is the

desired product. The product contains 6.90% phosphorus (6.75% theory) and 2.92% nitrogen (2.97% theory).

(D-4) Phosphorus-containing carboxylic ester

In one embodiment, the antiwear agent (D) is a phosphorus-containing carboxylic ester (D-4). The phosphorus-containing esters may be prepared by reaction of one of the above-described phosphorus acids, such as a dithiophosphoric acid, and an alpha, beta unsaturated carboxylic compounds, such as acrylic and methacrylic acids or esters. If the carboxylic acid is used, the ester may then be formed by subsequent reaction with an alcohol. The unsaturated carboxylic esters may contain from about 4 to about 40 carbon atoms, preferably 4 to about 24, more preferably 4 to about 12. Preferably, the unsaturated carboxylic acid is an allyl or vinyl ester of a carboxylic acid or an ester of an unsaturated carboxylic acid.

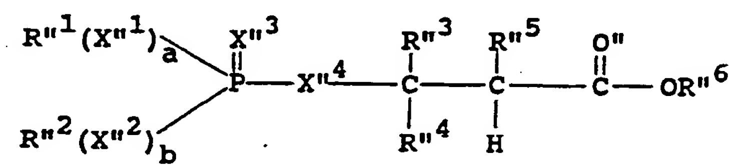
The vinyl ester of a carboxylic acid may be represented by the formula $R_6CH=CH-O(O)CR_7$ wherein R_6 is a hydrogen or hydrocarbyl group having from 1 to about 30 carbon atoms, preferably hydrogen or a hydrocargyl group having 1 to about 12, more preferably hydrogen and R_7 is a hydrocarbyl group having 1 to about 30 carbon atoms, preferably 1 to about 12, more preferably 1 to about 8. Examples of vinyl esters include vinyl acetate, vinyl 2-ethylhexanoate, vinyl butanoate, vinyl crotonate.

In another embodiment, the unsaturated carboxylic ester is an ester of an unsaturated carboxylic acid such as maleic, fumaric, acrylic, methacrylic, itaconic, citraconic acids and the like. In one embodiment, the ester is represented by the formula $R_8O-(O)C-HC=CH-C(O)OR_8$ wherein each R_8 is independently a hydrocarbyl group having 1 to about 18 carbon atoms, preferably 1 to about 12, more preferably 1 to about 8.

Examples of unsaturated carboxylic esters, useful in the present invention, include methylacrylate, ethyl-

acrylate, 2-ethylhexylacrylate, 2-hydroxyethylacrylate, ethylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, 2-hydroxypropylacrylate, ethylmaleate, butylmaleate and 2-ethylhexylmaleate. The above list includes mono- as well as diesters of maleic, fumaric and citraconic acids.

In one embodiment, the phosphorus-containing carboxylic ester (D-4) is represented by the formula:



wherein each X''^1, X''^2, X''^3 and X''^4 is independently oxygen or sulfur;

R''^1 and R''^2 are independently hydrocarbyl groups;

R''^3, R''^4 and R''^5 are independently hydrogen or hydrocarbyl groups;

R''^6 is a hydrocarbyl group; and

a and b are independently zero or 1.

X''^1 and X''^2 are preferably oxygen, and X''^3 and X''^4 are preferably sulfur.

Each R''^1 and R''^2 is independently a hydrocarbyl group of from 1 to about 50 carbon atoms, more preferably from 1 to about 30 carbon atoms, more preferably from 3 to about 18 carbon atoms, more preferably from 4 to about 8 carbon atoms. Each R''^1 and R''^2 is preferably independently an alkyl group. Examples of R''^1 and R''^2 include independently t-butyl, isobutyl, amyl, isooctyl, decyl, dodecyl, eicosyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphthyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylnaphthylalkyl groups, and the like.

Preferably each R''^3, R''^4 and R''^5 is independently a hydrogen or hydrocarbyl group of from 1 to about 50

carbon atoms. More preferably, each R''^3, R''^4 and R''^5 is independently a hydrogen; alkyl group of from 1 to about 22 carbon atoms; cycloalkyl groups of from about 4 to about 22 carbon atoms; or aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl group of from about 4 to about 34 carbon atoms.

R''^6 is preferably an alkyl group of from 1 to about 22 carbon atoms; a cycloalkyl group of from about 4 to about 22 carbon atoms; or an aromatic, alkyl-substituted aromatic or aromatic-substituted alkyl group of from about 4 to about 34 carbon atoms.

In a particularly preferred embodiment, each R''^1 and each R''^2 is independently an alkyl group of from about 3 to about 18 carbon atoms; X''^1 and X''^2 are oxygen; X''^3 and X''^4 are sulfur; R''^3, R''^4 and R''^5 independently are hydrogen or methyl; and n" is 1.

(D-5) Phosphorus-Containing Ether

In one embodiment, the antiwear agent (D) is the reaction product of a phosphorus acid and vinyl ether. The vinyl ether is represented by the formula R_8-CH_2=CH-OR_9 wherein each R_8 is hydrogen or a hydrocarbyl group having 1 to about 30, preferably 1 to about 24, more preferably 1 to about 12 carbon atoms and R_9 is a hydrocarbyl group having 1 to about 30 carbon atoms, preferably 1 to about 24, more preferably 1 to about 12. Examples of vinyl ethers include vinyl methylether, vinyl propylether, vinyl 2-ethylhexylether and the like.

(D-6) Dithiocarbamate Compounds

In one embodiment, the antiwear agent (D) is a dithiocarbamate-containing compound (D-6). The dithiocarbamate-containing compounds may be dithiocarbamate esters, dithiocarbamate amides, dithiocarbamic ethers, or alkylene-coupled dithiocarbamates. The dithiocarbamate amides, ether, and esters are prepared in a manner similar as that described above for phosphorus-containing amides and

esters. Generally, the dithiocarbamic acid is reacted with an unsaturated amide, ether, or ester to form the dithiocarbamate-containing compounds.

The dithiocarbamates used in making the dithiocarbamate-containing compound (D-6) are prepared by reacting an amine with carbon disulfide or carbonyl sulfide. The amines are generally any of the amines described above. Preferably, the amines are secondary amines. Specific amines include dimethyl amine, diethyl amine, dipropyl amine, dibutyl amine, diamyl amine, dihexyl amine and diheptyl amine. Nonsymmetrical amines may also be used and they include methylethyl amine, ethylbutyl amine, ethylamyl amine and the like. The unsaturated amide, ether, or esters are preferably alpha, beta unsaturated compounds. These compounds are described above. Preferably, these compounds include methylacrylate, ethylacrylate, 2-ethylhexylacrylate, 2-hydroxyethylacrylate, ethylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydryxypropylmethacrylate, 2-hydroxypropylacrylate, an acrylamide, and acrylonitrile, preferably acrylamides. Acrylamides include acrylamide, methacrylamide, bisacrylamide, bismethacrylamide, bis-methyleneacrylamide, N-hydroxymethylacrylamide, N-mercapto-methylacrylamide, N-(methyl, ethyl, bioether) acrylamide, and N-(methyl, ethyl, ether) acrylamide.

The dithiocarbamates are reacted with the unsaturated compounds at a temperature of about 25°C. to about 125°C., preferably about 50°C. to about 100°C., more preferably 70°C. to about 90°C. The reaction may be carrier out in the presence or absence of a solvent. Solvents include hydrocarbons such as toluene, xylene, hexane, heptane, kerosene, fuel oil or oils of lubricating viscosity as well as chlorohydrocarbons including chloroform, carbon tetrachloride and the like. Alcohols may also be used, such as methanol, ethanol, bropanol, butanol, 2-ethylhexanol and the like.

The following examples illustrate dithiocarbamate containing compounds (D-6) of the present invention.

EXAMPLE 11

A 1-liter flask is charged with 71g of acrylamide and 60 g of 95% ethanol. This mixture is stirred at room temperature for ¾ hour. An additional 40g of 95% ethanol is added to completely dissolve the acrylamide. To the solution is added 76g of CS_2. Diamylamine (157g) is added over 1.23 hours. An exotherm to 41°C. occurs. This mixture is heated and the temperature is maintained at 50°-55°C. for three hours. This mixture is subsequently vacuum stripped at 91°C. and 20 mm Hg to yield 113g of distillate. The residue is filtered through diatomaceous earth filter aid with a filtrate yield of 281g of clear, yellow, viscous liquid.

EXAMPLE 12

A 1-liter flask is charged with 172g of methyl-acrylate and 156g of CS_2. This mixture is stirred at room temperature and 146g of diethylamine are added over 2¾ hours, producing an exotherm to 62°C. The mixture is then held at 55°C. for 2½ hours and then is allowed to cool while standing overnight. The reaction mixture is then stirred and is heated to approximately 55°C. and is held at that temperature for two hours. The mixture is then vacuum stripped at 73°C. at 9 mm Hg. The residue is then filtered through diatomaceous earth filter aid to give 447g of a clear, brown filtrate.

In one embodiment, the dithiocarbamate-containing compound (D-6) is an alkylene-coupled dithiocarbamate. Alkylene-coupled dithiocarbamates may be represented by the formula

$$R_9(R_{10})N-\overset{\overset{\displaystyle S}{\|}}{C}-S-R_{11}-S-\overset{\overset{\displaystyle S}{\|}}{C}-N(R_{10})R_9$$

wherein R_9, R_{10} and R_{11} are defined below.

Each R_9 is independently a hydrogen; a hydrocarbyl group having from 1 to about 18 carbon atoms, preferably 1 to about 10, more preferably 1 to about 6; or R_9 taken together with R_{10} and the nitrogen atom form a five, six or seven member heterocyclic group. Preferably, each R_9 is hydrogen or an alkyl group, more preferably hydrogen or a propyl, butyl, amyl or hexyl group, more preferably a butyl group. The above list encompasses all stereo arrangements these groups, including isopropyl, n-propyl, sec-butyl, isobutyl, and n-butyl.

Each R_{10} is independently a hydrocarbyl group having from 1 to about 18 carbon atoms, or R_{10} taken together with R_9 and the nitrogen atom form a five, six or seven member heterocyclic group. When R_{10} is a hydrocarbyl group, it is defined the same as when R_9 is a hydrocarbyl group.

When R_9 and R_{10} are taken together with a nitrogen atom to form a five, six or seven member heterocyclic group, the heterocyclic group is a pyrrolidinyl, a piperidinyl, a morpholinyl or a piperazinyl group. The heterocyclic group may contain one or more, preferably one to three alkyl substituents on the heterocyclic ring. The alkyl substituents preferably contain from about one to about six carbon atoms. Examples of heterocyclic groups include 2-methylmorpholinyl, 3-methyl-5-ethylpiperidinyl, 3-hexylmorpholinyl, tetramethylpyrrolidinyl, piperazinyl, 2,5-dipropylpiperazinyl, piperidinyl, 2-butylpiperazinyl, 3,4,5-triethylpiperidinyl, 3-hexylpyrrolidinyl, and 3-ethyl-5-isopropylmorpholinyl groups. Preferably, the heterocyclic group is a pyrrolidinyl or piperidinyl group.

In one embodiment, each R_9 is independently a hydrogen, or a hydrocarbyl group and each R_{10} is independently a hydrocarbyl group. In another embodiment, one R_9 and R_{10} taken together with a nitrogen atom form a five, six or seven member heterocyclic group while the other R_9 is independently a hydrogen or a hydrocarbyl group and the

other R_{10} is a hydrocarbyl group. In another embodiment, each R_9 and R_{10} taken together with the nitrogen atom form a five, six or seven member heterocyclic group.

R_{11} is a hydrocarbylene group having from 1 to about 10 carbon atoms, preferably 1 to about 4, more preferably 1 or 2. Preferably, R_{11} is an alkylene, arylene, alkarylene, or arylalkylene. In one embodiment, R_{11} is an alkylene group, preferably, a methylene or ethylene group, more preferably methylene.

In one embodiment, R_{11} is an arylene group, alkarylene group, or arylalkylene group having from 6 to about 10 carbon atoms, preferably 6 to about 8. Preferably, R_{11} is a phenylmethylene, phenylethylene, phenyldiethylene, phenylene, tolylene, etc.

The alkylene-coupled dithiocarbamates useful in the present invention may be prepared by the reaction of a salt of a dithiocarbamic acid with a suitable dihalogen containing hydrocarbon in the presence of a suitable reaction medium. Suitable reaction media include alcohols, such as ethanol and methanol; ketones, such as acetone or methylethylketone; ethers, such as dibutylether or dioxane; and hydrocarbons, such as petroleum ether, benzene and toluene. The reaction is generally carried out at a temperature within the range of about 25°C to about 150°C, more preferably about 25°C to about 100°C.

U.S. Patent 3,876,550 issued to Holubec describes lubricant compositions containing alkylene dithiocarbamic compounds. U.S. Patents 1,726,647 and 1,736,429 issued to Cadwell describes phenylmethylene bis(dithiocarbamates) and methods of making the same. These patents are incorporated by reference for their teachings related to dithiocarbamate compounds and methods for preparing the same.

The following example relates to dithiocarbamate containing compounds (D-6).

EXAMPLE 13

A reaction vessel is charged with 1000 parts (7.75 moles) of di-n-butylamine, 650 parts (8.1 moles) of a 50% aqueous solution of sodium hydroxide, and 1356 parts of water. Carbon disulfide (603 parts, 7.9 moles) is added to the above mixture while the temperature of the reaction mixture is maintained under about 63°C. After completion of the addition of the carbon disulfide, methylene dichloride (363 parts, 4.3 moles) is added over four hours while the reaction mixture is heated to 88°C. After the addition of methylene dichloride, the mixture is heated for an additional three hours at a temperature in the range of 85°C-88°C. The stirring is stopped and the aqueous phase is drained off. The reaction mixture is stripped to 150°C and 50 millimeters of mercury. The residue is filtered. The filtrate has 6.5% nitrogen and 30.0% sulfur.

Lubricating Compositions

The inventors have discovered that the combination of (A) a basic alkali or alkaline earth metal salt of an acidic organic compound, (B) a metal deactivator other than a dimercaptothiadiazole and (C) a hydrocarbyl phosphite provide thermal stability to lubricating compositions. The basic metal salt (A) and hydrocarbyl phosphite (C) must be present so that the ratio of equivalents of (A) based on total base number to equivalents of phosphite (C) based on phosphorus atoms must be at least one. An excess of basic metal salt (A) may be used, i.e. the ratio of total base number to equivalents of phosphite (C) may be greater than one.

The compositions of the present invention may be used in lubricating compositions and functional fluids. The compositions are useful in power transfer fluids, including hydraulic, gear, automatic transmission and tractor fluids, preferably hydraulic fluids.

In one embodiment, the compositions are free of zinc dithiophosphates. The use of the term "free of" refers to compositions which are substantially free of zinc dithiophosphate. In another embodiment, the compositions are free of phosphorus containing ester or amide. In another embodiment, the compositions are free of zinc.

The lubricating compositions and functional fluids employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, solvent or acid treated mineral oils, and oils derived from coal or shale. Synthetic lubricating oils include hydrocarbon oils, halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silcon-based oils.

Specific examples of the oils of lubricating viscosity are described in U.S. Patent 4,326,972 and European Patent Publication 107,282, both herein incorporated by reference for their disclosures relating to lubricating oils. A basic, brief description of lubricant base oils appears in an article by D. V. Brock, "Lubricant Base Oils", Lubrication Engineering, Volume 43, pages 184-185, March, 1987. This article is herein incorporated by reference for its disclosures relating to lubricating oils. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

The overbased metal salt (A) is generall present in an amount from about 0.005%, preferably about 0.01%, more preferably about 0.075% up to about 5%, preferably about 1%, more preferably about 0.3% by weight of the total composition. The metal deactivator (B) is generally

present in an amount from about 0.001%, preferably 0.005%, more preferably about 0.05% up to about 0.2%, preferably about 0.1%, more preferably about 0.05% by weight of the total composition. The phosphite (C) is generally present in an amount from about 0.01%, preferably about 0.05%, more preferably about 0.075% up to about 5%, preferably about 1%, more preferably about 0.5% by weight of the total composition.

In another embodiment, the compositions of the present invention include from about 0.01%, preferably about 0.05%, more preferably about 0.075% up to about 5%, preferably about 2%, more preferably about 1% by weight of a sulfur-, phosphorus- or sulfur- and phosphorus-containing antiwear agent (D). When the basic metal salt (A) is a basic magnesium salicylate then (D) is present in an amount up to about 0.40% by weight of the total composition, preferably from about 0.01%, more preferably about 0.05%, up to about 0.4%, preferably about 0.3%, more preferably about 0.25%.

The above combination of the present invention may be used, in lubricants, in functional fluids or in concentrates, by themselves or in combination with any other known additive which includes, but is not limited to dispersants, antioxidants, anti-wear agents, extreme pressure agents, emulsifiers, demulsifiers, friction modifiers, anti-rust agents, corrosion inhibitors, viscosity improvers, pour point depressants, dyes, and solvents to improve handleability which may include alkyl and/or aryl hydrocarbons. These additives may be present in various amounts depending on the needs of the final product.

Dispersants include but are not limited to hydrocarbon substituted succinimides, succinamides, esters, and Mannich dispersants as well as materials functioning both as dispersants and viscosity improvers. These dispersants are described above as acylated nitrogen com-

pounds, hydrocarbyl substituted amines and Mannich reaction products. The dispersants listed above may be post-treated with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon substituted succinic anhydride, nitriles, epoxides, boron compounds, phosphorus compounds and the like.

Antioxidants, corrosion inhibitors, extreme pressure and anti-wear agents include but are not limited to chlorinated aliphatic hydrocarbons; boron-containing compounds including borate esters; and molybdenum compounds.

Viscosity improvers include but are not limited to polyisobutenes, polymethyacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins and multifunctional viscosity improvers.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. See for example, page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lesius-Hiles Company Publishers, Cleveland, Ohio, 1967).

Anti-foam agents used to reduce or prevent the formation of stable foam include silicones or organic polymers. Examples of these and additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

These and other additives are described in greater detail in U.S. Patent 4,582,618 (column 14, line 52 through column 17, line 16, inclusive), herein incorporated by reference for its disclosure of other additives that may be used in combination with the present invention.

The following are examples of lubricants useful in the present invention.

Table I

	Lubricants (% by weight)									
	A	B	C	D	E	F	G	H	I	J
Dibutylhydrogen phosphite	0.1	0.1			0.1		0.1			0.1
Triphenyl phosphite			0.075					0.1		
Di-2-ethylhexyl phosphite				0.09		0.1			0.1	
Tolytriazole	0.01	0.01			0.01	0.008	0.01		0.01	0.01
Benzotriazole			0.01	0.01				0.01		
Octyl imidazole										
Sodium sulfonate (metal ratio=20, total base number =440, and 36% by weight 100 neutral mineral oil)				0.08						
Calcium sulfonate (metal ratio=20, total base number =400, and 44% by weight 100 neutral mineral oil)			0.075					0.1		
Calcium phenate (metal ratio=5, total base number =250, and 30% by weight 100 neutral mineral oil)						0.1				

Table I

Lubricants (% by weight) (Continued)

	A	B	C	D	E	F	G	H	I	J
Magnesium sulfonate (metal ratio=15; total base number =400; and 32% by weight 100 neutral mineral oil)					0.1				0.1	0.1
Magnesium salicylate (metal ratio=6; total base number =345; and 38% by weight 100 neutral mineral oil)	0.1	0.1					0.1			
Reaction product of propylene oxide and tetrapropenyl succinic acid	0.05				0.05		0.05		0.05	0.05
Phosphorus-containing amide derived from diisooctyl dithiophosphoric acid, acrylamide and paraformaldehyde			0.15							

Table I

Lubricants (% by weight) (Continued)

	A	B	C	D	E	F	G	H	I	J
Phosphorus-containing carboxylic ester derived from isobutyl-amyl dithiophosphoric acid, and methylacrylate, post-treated with propylene oxide				0.1					0.2	
Dithiocarbamate containing ester derived from dibutyldithiocarbamate and methylacrylate				0.1		0.2				
Methylene-bis(dibutyl dithiocarbamate)								0.2		
Tricresyl phosphate	0.2	0.15			0.2		0.2			
Product of Example 7		0.5		0.25		0.25				
2,6-di-t-butyl phenol	0.25			0.25	0.25		0.25	0.5		
Di(nonylphenyl)amine	0.25		0.5		0.25	0.25	0.25		0.5	0.5
Mineral oil	*	*	*	*	*	*	*	*	*	*

*=Balance

Table I

Lubricants (% by weight)

	K	L	M	N	O
Dibutylhydrogen phosphite	0.03	0.03		0.05	
Triphenyl phosphite			1.0	0.10	0.2
Di-2-ethylhexyl phosphite					
Tolytriazole	0.005		0.05	0.005	0.01
Benzotriazole					
Octyl imidazole		0.05			
Sodium sulfonate (metal ratio=20, total base number =440, and 36% by weight 100 neutral mineral oil)					
Calcium sulfonate (metal ratio=20, total base number =400, and 44% by weight 100 neutral mineral oil)	0.25	0.4	2.0		
Calcium phenate (metal ratio=5, total base number =250, and 30% by weight 100 neutral mineral oil)					

Table I

Lubricants (% by weight) (Continued)

	K	L	M	N	O
Magnesium sulfonate (metal ratio=15; total base number =400; and 32% by weight 100 neutral mineral oil)				1.0	0.4
Magnesium salicylate (metal ratio=6; total base number =345; and 38% by weight 100 neutral mineral oil)					
Reaction product of propylene oxide and tetrapropenyl succinic acid	0.05	0.05	0.05	0.05	0.05
Phosphorus-containing amide derived from diisooctyl dithiophosphoric acid, acrylamide and paraformaldehyde					

Table I

Lubricants (% by weight) (Continued)

	K	L	M	N	O
Phosphorus-containing carboxylic ester derived from isobutyl-amyl dithiophosphoric acid, and methylacrylate, post-treated with propylene oxide					
Dithiocarbamate containing ester derived from dibutyldithiocarbamate and methylacrylate					
Methylene-bis(dibutyl dithiocarbamate)					
Tricresyl phosphate					
Product of Example 7		1.0	0.05	1.0	0.25
2,6-di-t-butyl phenol					
Di(nonylphenyl)amine					
Mineral oil					

*=Balance

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

CLAIMS

1. A composition, comprising:

(A) at least one basic alkali or alkaline earth metal salt of an acidic organic compound or mixtures thereof;

(B) at least one metal deactivator other than dimercaptothiadiazole or derivatives thereof; and

(C) at least one hydrocarbyl phosphite, wherein the ratio of the equivalents of (A) based on total base number to the equivalents of (C) based on phosphorus atoms is at least one,

provided that the composition is free of zinc dithiophosphate and

provided that when (A) is a basic magnesium salicylate then the composition contains (D) up to about 0.40% by weight of a sulfur-, phosphorus- or sulfur- and phosphorus-containing antiwear agent.

2. The composition of claim 1, wherein the acidic organic compound is a sulfonic acid, carboxylic acid or phenol.

3. The composition of claim 1, wherein the acidic organic compound is a salicylic acid.

4. The composition of claim 1, wherein the metal salt (A) is a basic metal salt having a metal ratio of about 1.1 to about 40.

5. The composition of claim 1, wherein the metal of the metal salt (A) is an alkaline earth metal.

6. The composition of claim 1, wherein the metal of the metal salt (A) is magnesium.

7. The composition of claim 1, wherein the metal salt (A) is a basic magnesium sulfonate.

8. The composition of claim 1, wherein the metal salt (A) is a basic magnesium salicylate.

9. The composition of claim 1, wherein the metal deactivator (B) is a triazole.

10. The composition of claim 1, wherein the metal deactivator (B) is tolytriazole or benzotriazole.

11. The composition of claim 1, wherein each hydrocarbyl group of the phosphite (C) independently contains from 1 to about 30 carbon atoms.

12. The composition of claim 1, wherein the phosphite (C) is dihydrocarbylhydrogen phosphite or tri-hydrocarbylphosphite.

13. The composition of claim 1, wherein the phosphite (C) is di- or tributyl phosphite, di- or tri-phenyl phosphite; or di- or trioctyl phosphite.

14. The composition of claim 1, wherein the phosphite (C) is dibutyl hydrogen phosphite.

15. The composition of claim 1, wherein the phosphite (C) is a trialkyl or triaryl trithiophosphite wherein each alkyl group independently has from 1 to about 30 carbon atoms and each aryl group independently has from 6 to about 30 carbon atoms.

16. The composition of claim 1, wherein the phosphite (C) is a triphenyl trithiophosphite.

17. The composition of claim 1, further comprising from about 0.01% to about 5% by weight of the composition of (D) a sulfur-, phosphorus-, or sulfur- and phosphorus-containing antiwear agent other than (C) the hydrocarbyl phosphite.

18. The composition of claim 1, wherein (D) the antiwear agent (D) is a sulfurized organic compound, a hydrocarbyl phosphate, a phosphorus-containing amide, ether, or ester, or a dithiocarbamate-containing compound.

19. The composition of claim 1, wherein (D) is a hydrocarbyl phosphate.

20. The composition of claim 19, wherein the hydrocarbyl groups of the phosphate (D) each independently contain from about 2 to about 18 carbon atoms.

21. The composition of claim 19, wherein the phosphate is tricresyl phosphate.

22. The composition of claim 1, wherein (D) is a phosphorus-containing carboxylic ester or amide prepared by reacting a phosphorus acid with an unsaturated amide or ester.

23. The composition of claim 1, wherein (D) is a dithiocarbamate-containing compound selected from hydrocarbylene-coupled dithiocarbamates, sulfur-coupled dithiocarbamates and reaction products of dithiocarbamic acids or salts thereof with unsaturated acids, esters or amides.

24. The composition of claim 1, wherein (D) is a sulfurized organic compound selected from olefins, fatty acids, fatty oils, fatty esters, turpenes, Diels-Alder adducts and mixture thereof.

25. The composition of claim 1, wherein the metal salt (A) is present in an amount from about 0.005% to about 5% by weight; the metal deactivator (B) is present in an amount from about 0.001% to about 0.2% by weight; and the phosphite (C) is present in an amount from about 0.01% to about 5% by weight wherein all amounts are based on the total weight of the composition.

26. The composition of claim 1, wherein the composition is free of phosphorus-containing ester or amide.

27. A composition, comprising:

(A) at least one overbased magnesium carboxylate or sulfonate;

(B) tolytriazole or benzotriazole; and

(C) at least one hydrocarbyl phosphite wherein the hydrocarbyl groups of the phosphite independently contain from 1 to about 18 carbon atoms, wherein the ratio

of equivalents of (A) based on total base number to the equivalents of (C) based on phosphorus atoms is at least one,

provided the composition is free of zinc dithiophosphate and

provided that when (A) is an overbased magnesium salicylate then the composition contains from 0 to about 0.30 percent by weight of (D) a sulfur-, phosphorus-, or sulfur- and phosphorus-containing antiwear agent.

28. The composition of claim 27, wherein the carboxylate is a salicylate.

29. The composition of claim 27, wherein the phosphite (C) is di- or tributyl phosphite, di- or triphenyl phosphite; or di- or trioctyl phosphite.

30. The composition of claim 29, wherein (D) the antiwear agent is a sulfurized organic compound, a hydrocarbyl phosphate, a phosphorus-containing amide, ether or ester, or a dithiocarbamate-containing compound.

31. The composition of claim 30, wherein (D) is a sulfurized organic compound selected from olefins, fatty acids, fatty oils, fatty esters, turpenes, Diels-Alder adducts and mixtures thereof.

32. The composition of claim 30, wherein (D) is a hydrocarbyl phosphate.

33. The composition of claim 32, wherein the hydrocarbyl phosphate is tricresyl phosphate.

34. A lubricating composition or functional fluid, comprising a major amount of an oil of lubricating viscosity and the composition of claim 1.

35. A lubricating composition or functional fluid, comprising a major amount of an oil of lubricating viscosity and the composition of claim 27.

36. The composition of claim 34, wherein the lubricating composition or functional fluid is a hydraulic fluid.

37. The composition of claim 35, wherein the lubricating composition or functional fluid is a hydraulic fluid.

38. The composition of claim 34, wherein the lubricating composition is a gear oil.

39. The composition of claim 35, wherein the lubricating composition is a gear oil.

40. A concentrate, comprising an oil of lubricating viscosity and a major amount of the composition of claim 1.

41. A concentrate, comprising an oil of lubricating viscosity and a major amount of the composition of claim 27.

INTERNATIONAL SEARCH REPORT

International Application No ‑ ‑T/US 92/02824

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10M163/00; C10M141/10

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10M

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	WO,A,8 904 358 (THE LUBRIZOL CORP.) 18 May 1989 cited in the application	1-14,17, 18,22, 23, 25-3034-41
	see page 90, paragraph 1	
Y	see page 101 - page 102; claims 1-70	15,19-21

X	EP,A,0 316 610 (IDEMITSU KOSAN CO. LTD) 24 May 1989	1,2, 9-13,17, 1823,25, 26, 34-36, 38,40
	see page 5, line 50 - line 54	
Y	see page 9; claims 1,3; table 2	15,16, 19-21

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° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
31 AUGUST 1992	21. 09. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	ROTSAERT L.D.C.

1

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 384 639 (ETHYL CORP.) 29 August 1990 see page 2, line 22 - line 29 see page 3, line 20 - line 27 see page 3, line 57 - page 4, line 5; claim 1 ---	1-14, 25-29, 34-41 2
Y	GB,A,1 041 721 (ALBRIGHT&WILSON LTD) 7 September 1966 see page 5, line 29 - page 6, line 28; claims 1,3 see claims 1-18 ---	15,16
Y	FR,A,2 215 462 (ESSO RESEARCH AND ENGINEERING CO.) 23 August 1974 ---	19-21

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9202824
SA 61489

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/08/92
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		EP-A-	0351428	24-01-90
		JP-T-	2502027	05-07-90
EP-A-0316610	24-05-89	JP-A-	1225696	08-09-89
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		GB-A-	1415964	03-12-75
		NL-A-	7315445	29-07-74

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82